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DEPENDENCE OF PROPERTIES OF ACID-RESISTANT PRODUCTS ON THE MOLDING METHOD

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It is shown that the introduction of granodiorite from the Severskii granite quarry, the control of the granular composition of mixtures, and the use of a combined method for molding products based on Buskul'skoe clay make it possible to obtain an acid-resistant brick with steady properties and sizes, a higher strength (105 MPa), and a low shrinkage (6.3%). All properties of this product satisfy the requirements of GOST 474–90 for acid-resistant brick of class A.

Acid-resistant (chemically resistant) ceramic materials have to satisfy a number of requirements. Such materials should have high mechanical strength and heat resistance, as well as low porosity, since they serve in aggressive media [1, 2]. Their acid resistance should be high (at least 98% for products of class A) and their strength should be at least 55 MPa. The formation of structure and properties of acid-resistant products satisfying the specified requirements is a complicated technological process which is implemented using special raw materials and special techniques [2].

The method for producing acid-resistant materials that is the most common in domestic practice is plastic molding involving thorough processing of material. The main defect of plastic molding is the shrinkage of molded products in drying and, consequently, inconstancy of sizes and shape of articles.

In the semi-dry molding, air may become pressed inside a product, especially in molding finely dispersed mixtures. However, the advantage of semidry molding is that the molded product has a higher strength and more precise shape and size. The drying of such products is more facile and takes less time than in plastic molding. The disadvantage of semidry molding is a higher permeability compared with plastic molding, which impairs service properties.

The purpose of the present study is to investigate a combined method for producing refractories, which combines the advantages of plastic and semidry molding. Furthermore, the combined method allows for implementing the technology of acid-resistant products at factories producing chamotte by semidry molding.

Comparative tests of three molding methods (plastic, semidry, and combined) were performed using clay BR-3 from the Buskul'skoe deposit and chamotte (fraction 1 – 0 mm) produced by firing the specified clay (water absorption of chamotte 3%). The additive was granodiorite waste of the fraction below 0.5 mm from the Severskii granite quarry. The chemical composition of initial components is listed in Table 1.

The granulometric composition of clay BR-3 (%) is: particles over 0.06 mm — 1.00, 0.06 – 0.01 mm — 1.21, 0.01 – 0.005 mm — 0.22, 0.005 – 0.001 mm — 25.0, below 0.001 mm — 72.6. The granulometric composition of granodiorite is (%): particles of size over 5 mm — 0, 2.5 – 5.0 mm — 20.6, 1.25 – 2.50 mm — 14.9, 0.63 – 1.25 mm — 9.7, below 0.63 mm — 54.9.

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TABLE 1

Component	Samples	Weight content, %							
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	R_2O	calcination loss
Clay BR-3	Air-dry	49.04	29.13	2.98	0.24	0.82	1.33	0.52	12.60
	Calcined	56.40	33.50	3.43	0.28	0.94	1.53	0.60	–
Granodiorite	Air-dry	62.50	16.30	3.40	4.14	3.14	0.14	9.99	0.09
	Calcined	62.56	16.31	3.40	4.14	3.14	0.14	10.00	–

Buskul'skoe clay is highly dispersed with an increased content of ferric oxide, containing free silica in a finely dispersed state. The content of silica is determined by the dilatometric method, it is equal to 9.4%. The clay has medium plasticity, dries well, and has medium drying sensitivity.

The clay sinters intensely in the temperature interval of 1100 – 1150°C; in this case water absorption decreases from 7.9 to 1.9 %. An increase in temperature up to 1250°C lowers the water absorption from 1.9 to 0.1%.

Based on its mineral composition (determined by the DTA method) the clay belongs to the kaolinite-montmorillonite type with a small quantity (5 – 7%) of mixed-laminar formations.

Firing products containing kaolinite-montmorillonite clay is a complicated process [3], in which it is desirable to prevent the formation of cristobalite. The presence of cristobalite is the main reason for lowering the acid resistance and mechanical strength of products. Therefore, the purpose is to convert cristobalite into a melt or to bind it with Al_2O_3 and to produce as much mullite as possible.

A large amount of fine fractions and a high content of iron oxides facilitates sintering [2]. In this case it is not difficult to obtain products with low water absorption and water permissibility, but it is hard to achieve the desired phase composition to meet the standard requirements; therefore, special additives have to be added. The presence of 2.0 – 2.5% alkali oxides in mixtures ensures the desired properties in acid-resistant products, as at lower firing temperatures a melt is formed, whose structure facilitates the formation of mullite and impedes the formation of cristobalite. The additive that we studied was the waste generated at the Severskii granite quarry, which is a plutonic magmatic rock with a crystalline structure that represents an intermediate product between granite and quartz diorite.

Preliminary investigations established an optimum ratio of the clay, chamotte, and the specified waste equal to 65 : 20 : 15.

The batch formula was calculated taking into account the final chemical composition of the mixture regarding its content of alkali oxides (2.0 – 2.5%) and the ratio $R_2O : Fe_2O_3$ [3].

The waste was introduced into the batch in the form of a slip with 10% clay added. Milling was performed for 2 h in ceramic mills with the materials : balls : water ratio equal to 1 : 2 : 1 to a residue on a No. 0063 sieves not more than 14%. The density of the slip was 1.49 g/cm^3.

To prepare a plastic mixture, chamotte was moistened with the slip and part of the clay was added to it and then everything was mixed. After that the rest of the estimated water quantity (relative moisture 18%) and the rest of the clay was added. After thorough mixing, the samples were molded.

The batch preparation schedule in semidry molding was as follows: chamotte was moistened with the slip, part of the clay was added and mixed, and then the remaining clay and the estimated quantity of water (relative moisture 7%) was added. After mixing, the samples were molded by bilateral molding at a pressure of 40 MPa.

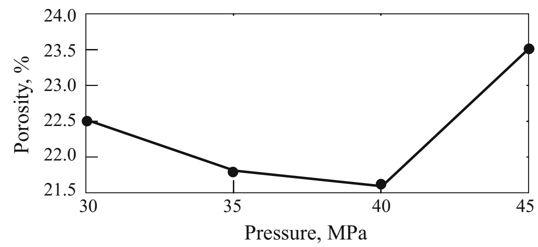

Fig. 1. Dependence of true porosity of samples on molding pressure.

The combined method is as follows. All components were mixed in preparing a plastic mixture, and then a briquette was molded from this mixture. The briquette was dried to a residual moisture not more than 5% and crushed to a grain size not more than 5 mm. The resulting powder was mixed with water to a moisture of 6 – 7% and then the samples were molded at a pressure of 40 MPa.

The optimum molding pressure for the combined molding method was selected experimentally. For this purpose cylindrical samples of diameter and height 36 mm were molded on a hydraulic press from a moistened mixture within the pressure range of 30 – 45 MPa with a step of 5 MPa. The compressed samples were dried at a temperature of 105 – 110°C and their apparent and true density was determined (according to GOST 2409–95 and GOST 2211–65, respectively). Figure 1 shows the variation of sample porosity with molding pressure.

To determine the pressure constants, we used the Berezhnoi equation:

$$E = a - b \log P,$$

where E is the true porosity, a and b are constants, and P is the molding pressure.

The physical meaning of these constants is as follows: a is the porosity of a mixture freely poured into a mold under a pressure of 0.5 kgf/cm^2 (including capillary and gravitation forces); the constant b characterizes the capacity of the mixture for consolidation under pressure in certain conditions; the value of this constant depends on the mixture properties, as well as on the shape and size of the molded articles and on molding conditions. The constants a and b for the given batch composition are equal to 31.00 and 5.83, respectively.

After drying, the samples were fired at a temperature of 1200°C with 1 h exposure at the final temperature. The properties of the samples are indicated in Table 2.

As expected, the semidry molding method does not ensure the required degree of sintering. The water absorption of samples is 9.9%.

The analysis of the properties of samples shows that the combined method yields products with stable properties and sizes, higher strength (105 MPa) and low shrinkage (6.3%).

TABLE 2

Molding method	Shrinkage, %		Water absorption, %	Open porosity, %	Apparent density, g/cm^3	Compressive strength, MPa	Acid resistance, %	Water imperme-ability, h
	air	total						
Plastic	5.2	11.9	4.6	9.9	2.16	81	97.5	> 48
Semidry	0.6	1.2	9.0	18.2	2.00	26	96.0	< 24
Combined	0.8	6.3	3.4	7.7	2.27	105	98.0	> 48
Requirements of GOST 474–90 to grade:								
A	–	–	6.0	–	–	55	97.5	> 48
B	–	–	6.8	–	–	50	97.5	> 36
C	–	–	8.0	–	–	35	96.0	> 24

TABLE 3

Mixture	Clay : cha-motte ratio	Shrinkage, %		Water absorption, %	Open porosity, %	Apparent density, g/cm^3	Compressive strength, MPa	Acid resistance, %	Water imperme-ability, h
		air	total						
K5	70 : 15	0.8	7.3	2.9	6.8	2.28	75	97.5	> 48
K4	65 : 20	0.8	6.3	3.4	7.7	2.27	105	98.0	> 48
K3	55 : 30	0.4	4.6	5.0	10.8	2.18	62	97.5	> 36
K2	45 : 40	0.4	3.2	6.5	13.5	2.10	53	97.0	< 24
K1	35 : 50	0.4	2.0	6.8	14.0	2.06	51	97.0	< 24

TABLE 4

Mixture	Content, %	
	free silica	cristobalite
K3	9.69	4.25
K4	10.31	3.96
K5	11.88	4.06

All parameters satisfy the requirements of GOST 474–90 for acid-resistant brick of class A.

The properties of the products depend on the content of the grog component in the mixture: a large content under firing leads to the formation of a porous structure, whereas a low content leads to high shrinkage. Therefore, we investigated the effect of chamotte content in mixtures on the properties of products.

For this purpose we prepared samples from batches with different ratios of clay to chamotte. The weight content of chamotte was equal to 15, 20, 30, 40, and 50%. The properties of samples fired at a temperature of 1200°C are listed in Table 3. It can be seen that samples of mixtures K5 and K4 have the optimum parameters satisfying the requirements of the state standard for acid-resistant brick of class A, whereas samples made from mixture K3 based on their water impermeability are attributed to class B. Samples from mixtures K2 and K1 do not satisfy the standard requirements regarding their water permeability. The fact that the mechanical strength decreases with decreasing content of chamotte (below 15%) is presumably related to the poor technological workability of the material due to its high clay content.

TABLE 5

Mixture	CLTE, 10^{-6} K^{-1}, in temperature interval, °C					
	20 – 100	20 – 200	20 – 300	20 – 400	20 – 500	500 – 600
K3	3.50	5.36	5.19	5.05	5.09	6.40
K4	3.67	5.25	5.04	4.99	5.01	6.75
K5	3.23	4.76	4.64	4.77	4.91	7.29

Dilatometric studies of samples from mixtures K3 – K5 show the presence of cristobalite and free silica in all mixtures. The content of free silica and cristobalite in fired materials is listed in Table 4 and the CLTE of the fired samples is indicated in Table 5.

Thermal resistance was determined on cube-shaped samples by heating them to 350°C and chilling them in water. All samples withstood more than 5 thermal cycles.

Thus, the introduction of granodiorite from the Severskii granite quarry, the regulation of the granular composition of mixtures, and the use of the combined method for preparing mixtures based on clay from the Buskul'skoe deposit yield an acid-resistant brick with steady size and properties, higher strength, and low shrinkage. All properties of this product satisfy the requirements of GOST 474–90 for acid-resistant brick of class A.

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